

- Chapter 16
Acids and Bases
- Some Definitions
- Arrhenius
 - Acid: Substance that, when dissolved in water, increases the concentration of hydrogen ions.
 - Base: Substance that, when dissolved in water, increases the concentration of hydroxide ions.

HCl is an Arrhenius Acid.

HCl gas is a molecular compound

It is very soluble in water and produces H^+ ions

Concentrated acid is 37% by mass and 12M in concentration.

NaOH is an Arrhenius Base

It is an ionic compound

It is soluble in water and produces OH^- ions

- Some Definitions
- Brønsted–Lowry
 - Acid: Proton donor
 - Base: Proton acceptor
- Certain substances can be either...

...it is amphoteric.



A Brønsted–Lowry acid...

...must have a removable (acidic) proton.

A Brønsted–Lowry base...

...must have a pair of nonbonding electrons.

- NH_3 is a Lowry base
- H^+ ion in water
- A H^+ ion is simply a proton with no surrounding electrons.
- So it can interact strongly with the nonbonding electron pairs of oxygen in water to form a hydronium ion H_3O^+
- Hydronium ion can form additional H bonds with water and form additional clusters like $H_5O_2^+$ and $H_9O_4^+$.
- What Happens When an Acid Dissolves in Water?
- Water acts as a Brønsted–Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed.
- What happens with NH_3

In Aqueous solutions



The Brønsted Lowry Acid base concept also applies to substances that are not in aqueous solutions:



This reaction occurs in gas phase.

- Conjugate Acids and Bases:
- From the Latin word *conjugare*, meaning “to join together.”
- Reactions between acids and bases always yield their conjugate bases and acids.
- **(a)** What is the conjugate base of each of the following acids: $HClO_4$, H_2S , PH_4^+ , HCO_3^- ?

- **(b)** What is the conjugate acid of each of the following bases: CN^- ,
- SO_4^{2-} , H_2O , HCO_3^- ?
- Acid and Base Strength
- Strong acids are completely dissociated in water.
 - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
 - Their conjugate bases are weak bases.
- Acid and Base Strength
- Substances with negligible acidity do not dissociate in water.
 - Their conjugate bases are exceedingly strong.
- Acid and Base Strength
- In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.
- Acid and Base Strength
- About Amphoteric and Amphiprotic
- In [chemistry](#), an **amphoteric** substance is one that can react as either an [acid](#) or [base](#)
- a substance is described as **amphiprotic** if it can both donate or accept a [proton](#)
- Auto ionization of Water
- As we have seen, water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.
- This is referred to as autoionization.
- This auto ionization of water is very limited
- About 2 molecules / 10^9 molecules.
- Ion-Product Constant

The equilibrium expression for this process is

$$K_c = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

This special equilibrium constant is referred to as the ion-product constant for water, K_w .

$$\text{At } 25^\circ \text{ C, } K_w = 1.0 \times 10^{-14}$$

At 25° C ,

$$K_w = [\text{OH}^-] [\text{H}_3\text{O}^+]$$

Remember H_3O^+ and H^+ both can be used interchangeably

$$= [\text{OH}^-] [\text{H}^+]$$

$$= 1.0 \times 10^{-14}$$

- You need to remember this value!

SAMPLE EXERCISE 16.4 Calculating [H+] for Pure Water

Calculate the values of $[\text{H}^+]$ and $[\text{OH}^-]$ in a neutral solution at 25°C .

SAMPLE EXERCISE 16.5 Calculate the concentration of H^+ (*aq*) in **(a)** a solution in which $[\text{OH}^-]$ is 0.010 M , **(b)** a solution in which $[\text{OH}^-]$ is $1.8 \times 10^{-9} \text{ M}$. *Note:* In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25°C .

- pH
- pH is defined as the negative base-10 logarithm of the hydronium ion concentration.

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

- pH
- In pure water,

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14}$$

- Because in pure water $[\text{H}_3\text{O}^+] = [\text{OH}^-]$,

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$$

- pH
- Therefore, in pure water,

$$\text{pH} = -\log (1.0 \times 10^{-7}) = 7.00$$

- An acid has a higher $[\text{H}_3\text{O}^+]$ than pure water, so its pH is <7
- A base has a lower $[\text{H}_3\text{O}^+]$ than pure water, so its pH is >7 .
- pH

These are the pH values for several common substances.

- If the pH is say, 3.76
- $\text{pH} = -\log [\text{H}^+] = 3.76$

$$\log [\text{H}^+] = -3.76$$

$$[\text{H}^+] = 10^{-3.76} = 1.7 \times 10^{-4}$$

- Other “p” Scales
- The “p” in pH tells us to take the negative log of the quantity (in this case, hydrogen ions).
- Some similar examples are
 - $\text{pOH} = -\log [\text{OH}^-]$
 - $\text{p}K_w = -\log K_w$

Since

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

If we take a $-\log$ of both sides

$$-\log [\text{H}_3\text{O}^+][\text{OH}^-] = -\log K_w$$

$$\log ab = \log a + \log b$$

therefore

$$\begin{aligned} (-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-]) &= -\log K_w \\ &= -\log(1.0 \times 10^{-14}) \\ &= 14.00 \end{aligned}$$

or, in other words,

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

- How Do We Measure pH?
- For less accurate measurements, one can use
 - Litmus paper
 - “Red” paper turns blue above $\sim \text{pH} = 8$
 - “Blue” paper turns red below $\sim \text{pH} = 5$
 - An indicator

- How Do We Measure pH?

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.

- Strong Acids
- You will recall that the seven strong acids are HCl, HBr, HI, HNO_3 , H_2SO_4 , HClO_3 Chloric acid, and HClO_4 Perchloric acid.
- These are, by definition, strong electrolytes and exist totally as ions in aqueous solution.
- For the monoprotic strong acids,

$$[\text{H}_3\text{O}^+] = [\text{acid}].$$

- Strong Bases
- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+} , Sr^{2+} , and Ba^{2+}).
- Again, these substances dissociate completely in aqueous solution.
- Dissociation Constants

- For a generalized acid dissociation, the equilibrium expression would be
- This equilibrium constant is called the acid-dissociation constant, K_a .
- Dissociation Constants

The greater the value of K_a , the stronger the acid.

SAMPLE EXERCISE 16.10 Calculating K_a and Percent Ionization from Measured pH

A student prepared a 0.10 M solution of formic acid (HCHO_2) and measured its pH using a pH meter. The pH at 25°C was found to be 2.38. **(a)** Calculate K_a for formic acid at this temperature. **(b)** What percentage of the acid is ionized in this 0.10 M solution?

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- Calculating K_a from the pH
- The pH of a 0.10 M solution of formic acid, HCOOH , at 25°C is 2.38. Calculate K_a for formic acid at this temperature.
- We know that
- Calculating K_a from the pH
- The pH of a 0.10 M solution of formic acid, HCOOH , at 25°C is 2.38. Calculate K_a for formic acid at this temperature.
- To calculate K_a , we need the equilibrium concentrations of all three things.
- We can find $[\text{H}_3\text{O}^+]$, which is the same as $[\text{HCOO}^-]$, from the pH.
- Calculating K_a from the pH

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$2.38 = -\log [\text{H}_3\text{O}^+]$$

$$-2.38 = \log [\text{H}_3\text{O}^+]$$

$$10^{-2.38} = 10^{\log [\text{H}_3\text{O}^+]} = [\text{H}_3\text{O}^+]$$

$$4.2 \times 10^{-3} = [\text{H}_3\text{O}^+] = [\text{HCOO}^-]$$

- Calculating K_a from pH

- Calculating K_a from pH
- Calculating Percent Ionization
- Percent Ionization = $\frac{[\text{H}_3\text{O}^+]}{[\text{HCOOH}]_{\text{initial}}} \times 100$
- In this example

$$[\text{H}_3\text{O}^+]_{\text{eq}} = 4.2 \times 10^{-3} \text{ M}$$

$$[\text{HCOOH}]_{\text{initial}} = 0.10 \text{ M}$$

- Calculating Percent Ionization
- Percent Ionization = $\frac{[\text{H}_3\text{O}^+]}{[\text{HCOOH}]_{\text{initial}}} \times 100$
- Calculating pH from K_a

Calculate the pH of a 0.30 M solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, at 25° C.



K_a for acetic acid at 25° C is 1.8×10^{-5} .

- Calculating pH from K_a
- The equilibrium constant expression is
- Calculating pH from K_a
- Calculating pH from K_a

Now,

- Calculating pH from K_a

Now

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log (2.3 \times 10^{-3})$$

$$\text{pH} = 2.64$$

- Percent ionization of $\text{HC}_2\text{H}_3\text{O}_2$

$$= \frac{0.0023\text{M}}{0.30} \times 100 = 0.77\%$$
- Something Very Important
- If the percent ionization of an acid is less than 5% then it can be taken as negligible.
- But if it is more than it, then it needs to be considered and the quadratic equations must be used to calculate the value of x.
- Strong vs. weak acid
- For 0.30 M solution of acetic acid the pH would be 2.64
- By comparison the pH of 0.30 M HCl would be

$$-\log [\text{H}^+] = -\log [0.30] = 0.52$$

Which is more acidic?

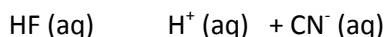
- The percent ionization of the *weak* acid decreases as the concentration increases.

SAMPLE EXERCISE 16.12 Using K_a to Calculate Percent Ionization

Calculate the percentage of HF molecules ionized in

- a 0.10 M HF solution,
- a 0.010 M HF solution.

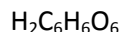
It is what we would expect from Le Châtelier's principle. • There are more "particles" or reaction components on the right side of the equation than on the left. Dilution causes the reaction to shift in the direction of the larger number of particles because this counters the effect of the decreasing concentration of particles.



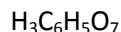
- Polyprotic Acids
- Have more than one acidic proton.

- If the difference between the K_a for the first dissociation and subsequent K_a values is 10^3 or more, the pH generally depends *only* on the first dissociation.

Ascorbic Acid



Citric Acid



- Weak Bases
Bases react with water to produce hydroxide ion.
- Weak Bases
The equilibrium constant expression for this reaction is
- Weak Bases

K_b can be used to find $[\text{OH}^-]$ and, through it, pH.

- pH of Basic Solutions

What is the pH of a 0.15 M solution of NH_3 ?

- pH of Basic Solutions
- pH of Basic Solutions

$$(1.8 \times 10^{-5})(0.15) = x^2$$

$$2.7 \times 10^{-6} = x^2$$

$$1.6 \times 10^{-3} = x$$

- pH of Basic Solutions

Therefore,

$$[\text{OH}^-] = 1.6 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log (1.6 \times 10^{-3})$$

$$\text{pOH} = 2.80$$

$$\text{pH} = 14.00 - 2.80$$

$$\text{pH} = 11.20$$

- K_a and K_b

K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

Therefore, if you know one of them, you can calculate the other.

Calculate

- the base-dissociation constant, K_b , for the fluoride ion (F^-);
 - the acid-dissociation constant, K_a , for the ammonium ion (NH_4^+).
- Acid-Base properties of salt solutions
 - Reactions of Anions with Water
 - Anions are bases.
 - As such, they can react with water in a hydrolysis reaction to form OH^- and the conjugate acid:
 - If the anion is a base of a strong acid then it will be a weak base and will have little tendency to abstract proton from water.
 - Consequently it will not affect the pH of the solution.
 - If the anion belongs to a weak acid it will consequently be a relatively strong base and will release the OH^- ion from water making it basic
 - Reactions of Cations with Water
 - Cations with acidic protons (like NH_4^+) will lower the pH of a solution, by donating a proton to the water molecule.



- Most metal cations that are hydrated in solution also lower the pH of the solution.

(details later)

- Reactions of Metal Cations with Water
- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O-H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic.
- Effect of Cations and Anions
 1. An anion that is the conjugate base of a strong acid will not affect the pH.
 2. An anion that is the conjugate base of a weak acid will increase the pH.
 3. A cation that is the conjugate acid of a weak base will decrease the pH.
- Effect of Cations and Anions
 4. Cations of the strong Arrhenius bases will not affect the pH.
 5. Other metal ions will cause a decrease in pH.
 6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the higher of the K_a and K_b values.
- Factors Affecting Acid Strength

Bond Polarity

Bond strength

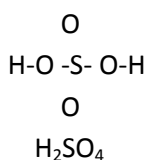
H-F though very polar, has a very strong bond with the bond enthalpy of 567 kJ / mol. So the HF acid is a weak acid.

Stability of the conjugate base. The more stable the conjugate base the stronger the acid

- Binary Acids
- Binary acids are acids between a proton and one more element.
- In general the H-X bond strength is the most important factor in determining the acid strength between the binary acids of the same group of the periodic table.
- The H-X Bond strength decreases as the element increases in size and so acidity increases down a group.
- Across a group the bond strength does not change much, so the bond polarity is the factor determining the acidity across a row.

Acidity increases as the electro negativity increases.

- Acidity increases from left to right across a row and from top to bottom down a group.
- Oxyacids



What makes this an acid and not a base

- Factors Affecting Acid Strength

Compounds in which an OH is bonded to another atom, Y,

If the Y was an electropositive metal then the compound would be a base

In oxyacids, the Y is a nonmetal and the more electronegative Y is, the more acidic the acid.

This happens because:

- a. the electron density is drawn towards Y and it makes the O-H bond weaker.
- b. The conjugate base of the acid is an anion and its stability increases as the electronegativity of Y increases.

- Factors Affecting Acid Strength

For a series of oxyacids, acidity increases with the number of oxygens.

- Carboxylic Acids

Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.

- Lewis Acids
- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- Lewis Bases
- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted–Lowry base is a Lewis base.
Lewis bases can interact with things other than protons, however.